

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
8 January 2004 (08.01.2004)

PCT

(10) International Publication Number
WO 2004/002972 A3

(51) International Patent Classification⁷: **C07D 301/10**

(74) Agent: **LEMUTH, Richard, F.**; Shell Oil Company. One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(21) International Application Number:
PCT/US2003/020095

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 24 June 2003 (24.06.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/392,679 28 June 2002 (28.06.2002) US

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **SHELL OIL COMPANY** [US/US]; Department of Intellectual Property, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **LOCKEMEYER, John, Robert** [US/US]; 3403 Stoney Mist Drive, Sugar Land, TX 77479 (US). **EVANS, Wayne, Errol** [US/US]; 1019 Lively Court, Richmond, TX 77479 (US). **REKERS, Dominicus, Maria** [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). **TE RAA, Arend, Jan** [NL/NL]; Koninginnegracht 23, NL-2514 AB The Hague (NL). **WERMINK, Thijs** [NL/NL]; Koninginnegracht 23, NL-2514 AB The Hague (NL).

Published:

— with international search report

(88) Date of publication of the international search report:
10 June 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A METHOD FOR THE START-UP OF AN EPOXIDATION PROCESS AND A PROCESS FOR THE EPOXIDATION OF AN OLEFIN

(57) Abstract: A method for the start-up of a process for the epoxidation of an olefin, which method comprises contacting a catalyst bed comprising a silver-based highly selective epoxidation catalyst, or a precursor of the catalyst comprising the silver in cationic form, with a feed comprising oxygen at a temperature of the catalyst bed above 260 °C for a period of at most 150 hours, and subsequently decreasing the temperature of the catalyst bed to a value of at most 260 °C, and a process for the epoxidation of an olefin, which process comprises contacting a catalyst bed comprising a silver-based highly selective epoxidation catalyst, or a precursor of the catalyst comprising the silver in cationic form, with a feed comprising oxygen at a temperature of the catalyst bed above 260 °C for a period of at most 150 hours, and subsequently decreasing the temperature of the catalyst bed to a value of at most 260 °C and contacting the catalyst with the feed comprising the olefin and oxygen.

BEST AVAILABLE COPY

WO 2004/002972 A3

THIS PAGE BLANK (USPTO)

INTERNATIONAL SEARCH REPORT

In. International Application No

PCT/US 03/20095

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D301/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 087 299 A (BAUM MATTHIAS ET AL) 11 July 2000 (2000-07-11) claim 1 column 7, lines 2-67 column 8, lines 46-54 examples 1-5	1-13
X	US 5 770 746 A (JEWSON JENNIFER D ET AL) 23 June 1998 (1998-06-23) claim 1 column 5, lines 61-64 column 7, lines 1-7 examples 1-10	1-6, 8-10, 12, 13
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

1 October 2003

Date of mailing of the international search report

20. 02. 2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Grassi, D

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/20095

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 874 879 A (LAURITZEN ANN M ET AL) 17 October 1989 (1989-10-17) cited in the application example 1	1-13
X	US 4 766 105 A (LAURITZEN ANN M) 23 August 1988 (1988-08-23) cited in the application column 19, lines 23-43; claim 1	1-13
X	GB 1 170 663 A (SHELL) 12 November 1969 (1969-11-12) examples I-IV	1-13

INTERNATIONAL SEARCH REPORT

ational application No.
PCT/US 03/20095

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1, 10
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-13 (part)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1,10

Present claims 1 and 10 relate to an extremely large number of possible methods. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the methods according to claim 2 where the catalyst is defined more specifically.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-13(part)

Process in which ethylene is epoxidised (claim 7) in the presence of a silver catalyst comprising a Group IA metal and one or more dopants selected from Re, Mo and W (claim 2).

2. claims: 1-6,8-10,12,13(all part)

Process in which an aromatic olefin is epoxidised (page 10) in the presence of a silver catalyst comprising a Group IA metal and one or more dopants selected from Re, Mo and W (claim 2).

3. claims: 1-6,8-10,12,13(all part)

Process in which a di-olefin is epoxidised (page 10) in the presence of a silver catalyst comprising a Group IA metal and one or more dopants selected from Re, Mo and W (claim 2).

4. claims: 1-6,8-10,12,13(all part)

Process in which 1-butene, 2-butene or isobutene is epoxidised (page 10) in the presence of a silver catalyst comprising a Group IA metal and one or more dopants selected from Re, Mo and W (claim 2).

5. claims: 1-6,8-10,12,13(all part)

Process in which propylene is epoxidised (page 10) in the presence of a silver catalyst comprising a Group IA metal and one or more dopants selected from Re, Mo and W (claim 2).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/20095

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6087299	A	11-07-2000	DE 19803890 A1	05-08-1999
			CA 2260433 A1	31-07-1999
			EP 0933130 A2	04-08-1999
			JP 11262664 A	28-09-1999
			PL 331058 A1	02-08-1999
			SK 12699 A3	14-02-2000
US 5770746	A	23-06-1998	AU 8018998 A	04-01-1999
			BR 9810264 A	12-09-2000
			CN 1107063 B	30-04-2003
			DE 69805067 D1	29-05-2002
			DE 69805067 T2	12-12-2002
			WO 9858920 A1	30-12-1998
			EP 0989976 A1	05-04-2000
			ES 2175722 T3	16-11-2002
			JP 2002504911 T	12-02-2002
US 4874879	A	17-10-1989	AU 616551 B2	31-10-1991
			AU 3892189 A	15-02-1990
			BR 8903658 A	13-03-1990
			CA 1329470 C	17-05-1994
			CN 1040794 A ,B	28-03-1990
			DE 68920658 D1	02-03-1995
			DE 68920658 T2	03-08-1995
			EP 0352849 A1	31-01-1990
			ES 2068884 T3	01-05-1995
			JP 2104580 A	17-04-1990
			JP 2779956 B2	23-07-1998
			KR 134881 B1	22-04-1998
			TR 24812 A	26-03-1992
US 4766105	A	23-08-1988	AT 69977 T	15-12-1991
			AU 592478 B2	11-01-1990
			AU 8053987 A	05-05-1988
			BG 60854 B1	31-05-1996
			BR 8705810 A	31-05-1988
			CA 1304346 C	30-06-1992
			CN 87107194 A ,B	27-07-1988
			CS 8806977 A2	12-09-1990
			CS 8707729 A2	13-06-1990
			DE 3774999 D1	16-01-1992
			DK 560087 A	01-05-1988
			EG 18719 A	30-12-1993
			EP 0266015 A1	04-05-1988
			ES 2028860 T3	16-07-1992
			FI 874786 A ,B,	01-05-1988
			GR 3003662 T3	16-03-1993
			HU 47046 A2	30-01-1989
			IE 60557 B1	27-07-1994
			IL 84232 A	21-06-1992
			IN 169589 A1	16-11-1991
			JP 2619660 B2	11-06-1997
			JP 63126552 A	30-05-1988
			KR 9611047 B1	16-08-1996
			MX 170627 B	31-08-1993
			NO 874528 A ,B,	02-05-1988
			NZ 222342 A	27-09-1989
			PH 25304 A	30-04-1991

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/20095

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4766105	A		PL 268522 A1	08-12-1988
			PT 86038 A ,B	01-11-1987
			RO 100109 A2	02-12-1991
			SG 126392 G	19-02-1993
			SU 1831369 A3	30-07-1993
			TR 26675 A	05-07-1994
			US 4820675 A	11-04-1989
			US 4808738 A	28-02-1989
			YU 180088 A1	28-02-1990
			YU 197887 A1	31-12-1988
			ZA 8708013 A	29-06-1988
GB 1170663	A	12-11-1969	AT 288329 B	25-02-1971
			BE 712496 A	20-09-1968
			CH 496468 A	30-09-1970
			DE 1767012 B1	21-05-1970
			DE 1793572 A1	01-07-1971
			ES 351780 A1	16-06-1969
			ES 354886 A1	16-02-1970
			FR 1563264 A	03-03-1969
			NL 6803918 A	23-09-1968
			NO 118743 B	09-02-1970
			SE 329997 B	02-11-1970
			SE 364708 B	04-03-1974
			US 3563914 A	16-02-1971

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)